Section 2: Chemical Monitoring

Photos by Betsy Briggs at Lake Anna Photography and Alliance for the Chesapeake Bay

Chapter 4

Dissolved Oxygen

What is Dissolved Oxygen?

Oxygen is found in aquatic systems as dissolved oxygen (DO) which enters the systems from the atmosphere and from photosynthesis of aquatic plants (Figure 4-1). Currents and waves help introduce oxygen into the aquatic system due to more water being in contact with the atmosphere and better mixing of surface and deeper waters.

Why Monitor Oxygen?

Dissolved oxygen is one of the most important measures of water quality. An aquatic system with low levels of oxygen cannot support healthy populations of animal or plant life. If more oxygen is being used than is being introduced, organisms may weaken, move away, or die. Aquatic animals and plants use oxygen for respiration. Oxygen is also removed from the aquatic system through decomposition of organic material. Excessive nutrient levels from runoff, failing septic systems, or wastewater from sewage treatment plants can contribute to low dissolved oxygen levels by causing abundant growths of phytoplankton (microscopic plants and algae) called blooms. Living phytoplankton may deplete oxygen levels during the night and as the phytoplankton die, decomposition of the organic material by bacteria consumes oxygen.

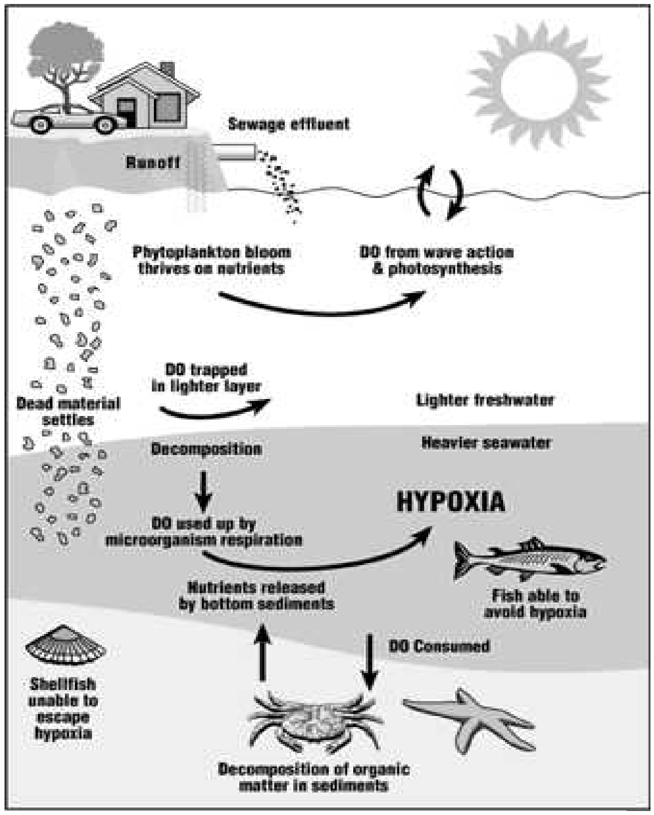

Figure 4-1. Processes affecting dissolved oxygen levels *(from Volunteer Estuary Monitoring: A Methods Manual, Second Edition).*

What Do Your Dissolved Oxygen Results Mean?

Dissolved oxygen (DO) is measured in mg/l (which is equivalent to parts per million or ppm). Aquatic organisms need a certain amount of dissolved oxygen in order to survive. The effects of low dissolved oxygen concentrations on aquatic organisms can be found in Table 4-1. Table 4-2 summarizes the water quality standards for dissolved oxygen in Virginia.

Table 4-1. Effects of Dissolved Oxygen on Aquatic Life

Levels of Dissolved Oxygen			
> 5 mg/l	**Between 3 – 5 mg/l**	**<3 mg/l – Hypoxia Occurs (low dissolved oxygen levels)**	**<0.5 mg/l - Anoxia Occurs (lack of dissolved oxygen)**
Level needed to support most aquatic life.	Aquatic organisms may become stressed.	Mobile organisms will move to areas of higher dissolved oxygen and immobile species may die.	Waters cannot support most aquatic life.

Table 4-2. Virginia Water Quality Standards for Dissolved Oxygen

	Most Waters	Stockable Trout Waters	Natural Trout Waters
Concentration of Dissolved Oxygen	Minimum 4 mg/l	Minimum 5 mg/l	Minimum 6 mg/l

Dissolved oxygen concentrations are affected by a number of variables such as time of day, depth, temperature, and salinity. Typically, DO concentrations of surface samples are highest around mid-day due to photosynthetic activity of aquatic plants. During the night, DO concentrations decline as DO is consumed through respiration while photosynthesis is halted due to the lack of sunlight. Therefore, DO levels are typically lowest in the early morning. Salt water cannot hold as much DO as fresh water (Figure 4-1). Lower DO concentrations are expected during the summer, since warm water cannot hold as much DO as cold water.

DO levels in lakes and estuaries can vary greatly with depth. During the summer months, vertical stratification (where warmer water is above colder water), can keep dissolved oxygen from reaching deeper waters. The deeper waters may maintain a low DO level until mixing occurs during storms or change of seasons.

The potential DO level, or DO saturation, is the maximum dissolved oxygen level possible under factors, such as temperature and salinity, that affect DO. Appendix 16 summarizes DO saturation levels at sea level at varying salinities and water temperatures. Percent saturation is the amount of oxygen in the water relative to the potential DO level. Percent saturation can be determined as follows:

$$\%\text{ Saturation} = \frac{\text{measured DO}}{\text{DO saturation (from Appendix 16)}} \times 100$$

Sampling and Quality Assurance/Quality Control (QA/QC) Considerations

Chapter 1 outlined a number of factors that every volunteer water quality monitoring program should consider. In addition to those summarized in Chapter 1, further considerations specific to monitoring for dissolved oxygen are discussed below.

When to Sample

Since DO fluctuates seasonally, it is best to sample DO throughout the year to obtain a more complete picture of water quality. If this is not possible, then sampling early spring through late fall may be preferred since critical DO levels are most common during warmer periods of the year. Since dissolved oxygen may fluctuate throughout the day, you may wish to sample about the same time of day so that your data does not show these fluctuations. This may be of particular interest if you are monitoring estuarine or lake waters and plan to track trends in DO levels.

Where to Sample

As described earlier, vertical stratification can affect DO levels at different depths. Since dissolved oxygen levels vary depending upon the depth, especially in the warmer months, volunteer monitoring programs may decide to measure DO at varying depths. This may be of particular interest if you are planning to monitor lakes or estuarine waters. Several water samplers designed to collect samples at different depths are shown in Figure 4-2. Meters attached to long cables can be used to collect profile data directly.

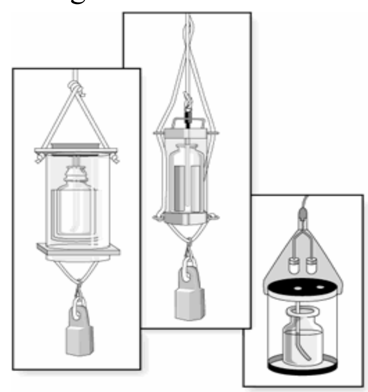

Figure 4-2. Dissolved oxygen samplers *(from Volunteer Estuary Monitoring: A Methods Manual, Second Edition).*

Choosing a Method

Dissolved oxygen can be easily and accurately measured using field test kits or meters. If using a meter, DO must be measured in the field. Some field test kits also require DO to be measured in the field, while others that are based on the Winkler titration method allow you to fix the water sample immediately upon collection and complete the analysis in a more desirable location within a few hours. The fixed samples must be stored in the dark without extreme temperature fluctuations.

Test Kits

Test kits may be more cost-effective than meters, but they do require replacement reagents once reagents expire or are used. Test kits also require proper storage, safety precautions, and proper disposal of waste. Monitors must follow protocols closely to ensure accurate results.

Test kits with increments greater than 0.2 mg/l or those not based upon a Winkler titration have limited uses, such as for educational purposes or to screen for potential problems. Winkler titration field test kits that measure DO in increments of 0.2 mg/l or less are acceptable for Department of Environmental Quality (DEQ) water quality assessments if the Quality Assurance Project Plan (QAPP) is approved by DEQ. Recommended quality assurance/quality control (QA/QC) measures include collecting and testing two water samples simultaneously to verify that the sampling is being done correctly. The difference between the two samples should be no more than ± 0.6 mg/l.

Volunteer measuring dissolved oxygen using a test kit *(photo courtesy of Alliance for the Chesapeake Bay)*.

Colorimeters

This instrument measures DO concentrations based upon the absorption spectrum. A colorimeter requires proper maintenance and calibration. The data collected with this instrument are not acceptable for use by DEQ for water quality assessments since this method has not been compared to other approved methods.

Meters

While meters are more expensive than test kits, they can provide accurate results and may allow collection of several parameters with one instrument. Data collected with meters are acceptable for DEQ water quality assessments if the QAPP is approved by DEQ. When choosing a meter, one that compensates for barometric pressure and includes a stirrer (the stirrer maintains a consistent flow over the probe's sensor) is recommended. In areas of good flow, a stirrer may not be necessary as long as the probe is gently swirled in the water and the flow is at least 1 foot per second. The results of the DO reading can be altered depending upon how fast the probe is swirled.

A meter must be calibrated at the beginning of each sampling day. The calibration results should be acceptable when compared to the chart of percent saturation in Appendix 16. If the results are not within ± 0.5 mg/l of the percent saturation chart, the data collected with the meter should be flagged.

Additionally, the calibration should be confirmed at the end of the sampling day (this is referred to as a "post check") to determine if the meter has drifted throughout the sampling day. The post check should be conducted similar to the calibration without pressing the calibration button. The value obtained should also be compared to Appendix 16 in the same manner as described in the previous paragraph.

Since a meter can sometimes malfunction, you should confirm the meter measurements with an approved method (a Winkler titration test kit with increments no greater than 0.2 mg/l will suffice) once for every 20 sampling events (this is referred to as a QA/QC check). The meter should read within $\pm$ 0.5 mg/l of the approved method. If the results are not within this range, the data collected with the meter should be flagged. All calibration, post check, and QA/QC data should be maintained.

Summary of Dissolved Oxygen Monitoring Methods

Method (Vendor and Catalogue #)	**Approximate Cost**	**Monitoring Level Depends Upon DEQ Approval of QAPP (see Appendix 9)**	**Organizations Using Method**
Winkler Titration Test Kit (Hach #1469-00)	$47.75 (100 tests)	I	None known
Winkler Titration Test Kit (LaMotte #7414 [acid powder] or #5860 [liquid acid])	$40.95 (50 tests)	I, II, or III	- Alliance for the Chesapeake Bay and affiliate organizations - Appomattox River Water Quality Monitoring Program (Clean Virginia Waterways / Longwood University) - Lake Anna Civic Association - Upper Rappahannock Watershed Stream Monitoring Program
Colorimeter	$150-$1000	I	- Friends of Powhatan Creek Watershed
Meters (a multi-parameter meter is more cost-effective than a single parameter meter)	$500-$1000 (DO only) $900-$5,000 (multi-parameter)	I, II, or III	- Friends of the Shenandoah River and affiliate organizations - Loudoun Wildlife Conservancy - Piedmont Region TMDL Initiative

Chapter 5

pH

What is pH?

pH is a term used to indicate the acidity or alkalinity of a solution as ranked on a scale from 0 to 14. Acidity increases as the pH decreases. The pH scale measures the concentration of hydrogen (H^+) and hydroxide (OH^-) ions, which make up water ($H^+ + OH^- = H_2O$). When both types ions are in equal concentration, the pH is 7.0 or neutral. Below 7.0, the water is acidic (there are more hydrogen ions than hydroxide ions). When the pH is above 7.0, the water is alkaline, or basic (there are more hydroxide ions than hydrogen ions).

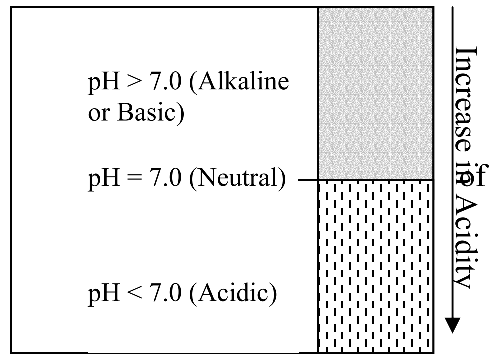

Figure 5-1. pH scale

Why Monitor pH?

pH affects many chemical and biological processes in the water. For example, different organisms flourish within different ranges of pH. Most aquatic organisms prefer a pH range between 6.5 and 8. A pH value outside this range reduces the diversity in the waterway because it stresses the physiological systems of most organisms and can reduce reproduction. Low pH can also allow toxic elements and compounds to dissolve and become more "available" for uptake by aquatic plants and animals. This can produce conditions that are toxic to aquatic life, particularly to sensitive species like rainbow trout. Changes in acidity can be caused by atmospheric deposition (including acid rain), weathering of surrounding rock, certain wastewater discharges, and the decomposition of plants and animals.

What Do Your pH Results Mean?

The water quality standard in Virginia defines acceptable pH as being between 6 and 9. pH values above or below this range indicate a violation of our state's water quality standards.

Since the pH scale is logarithmic, a drop in the pH by 1.0 unit is equivalent to a 10-fold increase in acidity. For example, a water sample with a pH of 5.0 is 10 times more acidic than one with a pH of 6.0, and a pH of 4.0 is 100 times more acidic than a pH of 6.0. Changes in pH of just one or two units can be very stressful to aquatic organisms.

Sampling and Quality Assurance/Quality Control (QA/QC) Considerations

Chapter 1 outlined a number of factors that every volunteer water quality monitoring program should consider. In addition to those summarized in Chapter 1, further considerations specific to monitoring for pH are discussed below.

When to Sample

Since pH fluctuates daily and seasonally, it is best to sample pH throughout the year to obtain a more complete picture of water quality. Because pH, like dissolved oxygen, may fluctuate throughout the day due to photosynthesis, you may wish to sample about the same time of day so as not to confuse daily fluctuations with pollution events. pH is increased by photosynthetic activity, which results in daily fluctuations, especially on sunny, warm days. This is of particular interest if you plan to track trends in pH levels.

Choosing a Method

pH is easily measured and must be measured in the field within 30 minutes (immediately is preferable) of collection of the water sample.

Test Kits

Test kits may be more cost-effective than meters, but they require replacement reagents once reagents expire or are used. Test kits also require proper storage, safety precautions, and proper disposal of waste. Monitors must follow protocols closely to ensure accurate results. pH test kits are cheap, safe and easy to use.

If you plan on using a field test kit with a limited pH range, you should first determine the average pH for your stream in order to select the correct range for your test kit. You can determine the average pH of your stream by either testing the stream with a wide range test kit (typically measures pH values from about 3-10) or locating existing pH data.

Volunteer measuring pH using a test kit *(photo courtesy of Alliance for the Chesapeake Bay).*

Since many citizen monitoring programs in Virginia use the LaMotte pH (liquid) test kits, the Department of Environmental Quality (DEQ) conducted a comparison study between these test kits and a reliable meter. These test kits were found to be useful for DEQ water quality assessments if the Quality Assurance Project Plan (QAPP) is approved by DEQ. However, DEQ does not plan to list waters as impaired for pH based solely on these tests since the color determinations may have a degree of subjectivity.

Colorimeters

This instrument measures pH based upon the absorption spectrum. This instrument requires proper maintenance and calibration. The data collected with this instrument are not acceptable for use by DEQ since this method has not been compared to other approved methods.

Meters

While meters are more expensive than test kits, they can provide accurate results and may allow collection of several parameters with one instrument. Data collected with meters are acceptable for use by DEQ for water quality assessments if the QAPP is approved by DEQ.

A meter must have the ability for calibrations at a minimum of 2 well-separated pH values (2-point calibration) to meet DEQ's QA/QC requirements. pH meters should be calibrated with at least 2 standard pH buffers (solutions of known pH values) for the range where pH values usually occur. If the pH value is usually below 7, then calibration should be done with standard pH buffers 4 and 7. If pH value is usually above 7, then calibration should be done with buffers 7 and 10. Meters must be calibrated at the beginning of the sampling day.

A post check must be conducted at the end of the day to determine if the meter has drifted throughout the sampling day. A post check means that you take pH readings for the same buffers you used at the beginning of the sampling day (this is not a calibration). The results for each buffer must be within $\pm$ 0.2 units of the buffer value. If the results are not within this range, the data collected with that meter should be flagged. All calibration data should be maintained.

Summary of pH Monitoring Methods

Method (Vendor and Catalogue #)	**Approximate Cost**	**Monitoring Level Depends Upon DEQ Approval of QAPP (see Appendix 9)**	**Organizations Using Method**
Wide Range (3.0 – 10.0) Field Test Kit (LaMotte # 2117)	$33.00 (50 tests)	I or II	- Alliance for the Chesapeake Bay and affiliate organizations - Lake Anna Civic Association - Upper Rappahannock Watershed Stream Monitoring Program
Various narrow range field test kits (LaMotte #2105, 2107, 2109, 2110, 2111, 2112) Use appropriate range	$33.00 (50 tests)	I or II	- Alliance for the Chesapeake Bay and affiliate organizations - Appomattox River Water Quality Monitoring Program (Clean Virginia Waterways / Longwood University)
Hach Color Disk Field Test Kits (#1470-04, 1470-14, 1470-06, 1470-08, 1470-09)	$55.00 (200 tests)	I	None known
Colorimeter	$150-$1000	I	- Friends of Powhatan Creek Watershed
pH Tester (Oakton Testr 2) *Must use standard buffers for calibration *Testr 2 meets DEQ's QA/QC requirements while Testr 1 does <u>not</u>.	$75.00	I , II, or III	- Alliance for the Chesapeake Bay and affiliate organizations
Meters (a multi-parameter meter is more cost-effective than a single parameter meter) *Must use standard buffers for calibration	$200-$1000 (pH only) $900-$5,000 multi-parameter)	I, II, or III	- Friends of the Shenandoah River and affiliate organizations - Loudoun Wildlife Conservancy

Chapter 6

Nutrients

What Are Nutrients?

Nutrients are necessary for the survival and growth of aquatic plants which are the base of the food chain for all other aquatic organisms. Although a number of nutrients (such as nitrogen, phosphorus, silica, carbon, potassium, calcium, and magnesium) are needed by plants for growth and reproduction, nitrogen and phosphorus are the two of particular interest that are more commonly monitored by volunteer monitoring programs. Nitrogen and phosphorus are the nutrients that limit plant growth in most aquatic systems. In this manual, we are referring to nitrogen and phosphorus when we speak about *nutrients.* The different forms of nitrogen and phosphorus will be discussed in further detail later in this chapter in the section entitled *Sampling and Quality Assurance/Quality Control (QA/QC) Considerations.*

Why Monitor Nutrients?

Nutrient levels in an aquatic system vary depending upon temperature, rainfall, runoff, biological activity, and the flushing of the aquatic system. Nutrient levels are generally higher in the spring and early summer and impact the aquatic system in several ways. High nutrient levels can accelerate eutrophication of a waterway. Eutrophication is characterized by abundant growths of phytoplankton (microscopic plants and algae) called algal blooms that may block sunlight from submerged aquatic vegetation (see Chapter 10). These algal blooms result in lower dissolved oxygen levels as decomposition of their organic matter consumes the dissolved oxygen.

Nutrient concentrations in aquatic systems are influenced by both natural and human sources. Natural sources of nitrogen and phosphorus include decomposition of organic matter, nitrogen fixation of atmospheric nitrogen by certain bacteria and algae, and geologic formations rich in nitrogen or phosphorus. Human sources include discharges from wastewater treatment plants, stormwater runoff, livestock wastes, fertilizer runoff from lawns and agricultural fields, groundwater seepage from failing septic systems, planting of nitrogen fixing plants (such as clover or beans) in agricultural fields, and atmospheric deposition (including acid rain) from the burning of fossil fuels.

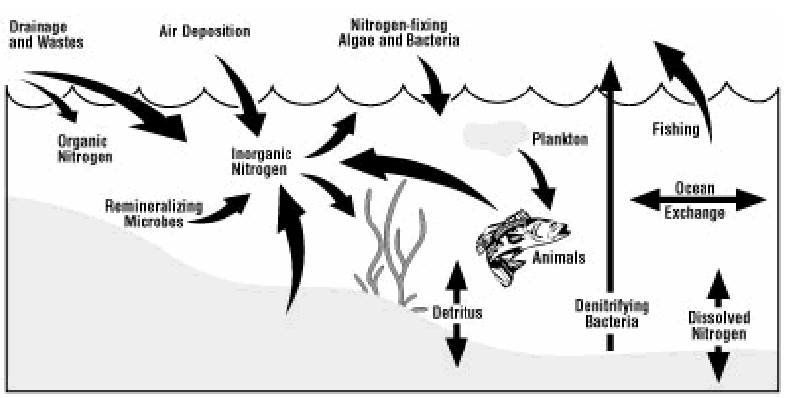

Figure 6-1. The nitrogen cycle *(from Volunteer Estuary Monitoring: A Methods Manual, Second Edition).*

What Do Your Nutrient Results Mean?

Developing nutrient criteria for the nation's waters is currently a hot issue. The debate centers on determining the limiting nutrient for a particular type of water in a particular ecoregion. Currently, Virginia has not yet adopted water quality standards for nutrients except for total ammonia as it relates to the toxicity to aquatic animals and nitrate for public drinking water supplies. Nitrate levels in public water supplies should not exceed 10,000 ug/l (micrograms/liter), or 10 mg/l.

The Virginia Department of Environmental Quality (DEQ) currently designates "nutrient enriched waters" where there is degradation due to excessive nutrients. For free-flowing streams, the maximum concentration for total phosphorus is 200 ug/l, or 0.20 mg/l; while it is only 50 ug/l, or 0.05 mg/l, for lakes. DEQ has recently begun the process of developing nutrient water quality standards. Nutrient water quality standards are scheduled to be adopted as follows: in 2005 for tidal tributaries to the Chesapeake Bay; in 2006 for lakes; and in 2007 for freshwater streams.

Sampling and Quality Assurance/Quality Control (QA/QC) Considerations

Chapter 1 outlined a number of factors that every volunteer water quality monitoring program should consider. In addition to those summarized in Chapter 1, several considerations specific to monitoring for nutrients are discussed below.

Different Forms of Nutrients

Nitrogen and phosphorus can be found in aquatic systems in many different forms, or species. While monitoring each individual species may help determine the source, it is important to remember that, when developed, Virginia's water quality standards may be for total nitrogen and total phosphorus.

Nitrogen Species

In aquatic systems, nitrogen exists in various inorganic chemical species (ammonia, nitrate and nitrite are all common components of synthetic fertilizers) and in particulate and dissolved organic and inorganic forms. Total nitrogen is a combination of nitrate, nitrite and total Kjhedal nitrogen (TKN). TKN is organic nitrogen, which is a complex mixture of compounds primarily derived from living and dead organisms.

Nitrification is the process whereby some bacteria convert ammonium to nitrite and then nitrite to nitrate. Since this process consumes oxygen, a system with low dissolved oxygen levels may experience increased concentrations of ammonia or nitrites. Nitrate is highly water-soluble and is easily carried by runoff. At high levels, nitrates and ammonia can be toxic. The natural level of ammonia and nitrate in discharge from wastewater treatment plants can be as high as 30 mg/l.

Phosphorus Species

In aquatic systems, phosphorus exists as orthophosphate (dissolved and inorganic), total phosphorus (dissolved and particulate), organic phosphate, and polyphosphate (from detergents). Orthophosphate is commonly measured and is found in fertilizers. Phosphate that is not associated with organic material is inorganic and this inorganic phosphorus is the form required by plants. Animals can use either organic or inorganic phosphate. Many phosphorus species attach to soil particles and are transported with sediment runoff. Phosphate in the aquatic system may bind to minerals in the sediment resulting in low phosphorus levels in the water. During conditions of no dissolved oxygen, bound phosphorus can be released into the water column triggering algal blooms.

Monitoring phosphorus is challenging because it involves measuring very low concentrations (0.01 mg/l or even lower). Even such very low concentrations of phosphorus can have a dramatic impact on streams. Methods that do not have detection limits this low can be used to identify potential problem areas.

When to Sample

Since nutrient concentrations are highly variable, it is best to sample for nutrients throughout the year and over a long period of time to obtain a more complete picture of water quality. Frequent sampling can also facilitate explaining variability in the data.

Choosing a Method

Choosing a method for nutrient analysis can pose a dilemma. Your decisions on the goals of your program and the intended data use will determine the method that you should use. At this time, laboratory analyses of nutrients are the only methods that yield results accurate enough for DEQ’s water quality assessments. Other methods may be used for educational or screening purposes.

Test Kits

Different forms of nutrients can be measured using test kits to screen for potential problem areas or “hot spots”. In general, nutrients are found in low concentrations that may be lower than the detection limits of the test kits. However, test kits that detect low levels can collect information about periodic increases in nutrient concentrations and help target areas where more advanced monitoring may be of interest. Data collected from nutrient test kits are not acceptable for use by DEQ for water quality assessments.

Colorimeters

This instrument measures nutrient concentrations based upon the absorption spectrum of the parameter. This instrument requires proper maintenance and calibration. Although this instrument has a lower detection limit than test kits, the data collected with this instrument are not acceptable for use by DEQ since the detection limit is not generally low enough to accurately measure nutrient concentrations.

Laboratory Analysis

Laboratory analysis of nutrients is the most accurate method for obtaining nutrient data. Even laboratory analysis requires strict quality assurance and quality control methods. Recommended QA/QC measures include:

- Proper Preservation: Table 6-1 describes acceptable preservation methods of water samples for lab analysis of various nutrient species.
- Field duplicates: A field duplicate is simply a second water sample taken at the same time as another sample to measure the reproducibility of the monitor, method and/or analyst. It is recommended that field duplicates are collected randomly for 10% of your samples (for a large sample size, 5% is acceptable). For example, if you collect 50 samples, you should collect field duplicates at 5 of those sites and label the duplicate samples.
- Field equipment blanks are only necessary if water samples are collected in a bucket or other sampling device and transferred into the sample container. A field equipment blank is simply a contaminant-free sample (distilled or deionized water) used to detect contamination of the collection device or cross-contamination between sites. A field equipment blank is collected and transferred in the same manner as the stream water sample. It is recommended that you collect field equipment blanks randomly for 10% of your samples (for a large sample size, 5% is acceptable).

Table 6-1. Preservation Methods for Laboratory Analysis of Various Nutrients

Parameter	**Chill on Ice to <4ºC** (immediately)	**Lower pH to < 2** (add 2 ml of sulfuric acid to 1 liter of sample)	**Freeze (in the lab)**	**Holding Time**
Total nitrogen	YES		YES	28 days
Ammonia/TKN	YES	YES		28 days
Nitrate/Nitrite	YES			48 hours
Total phosphorus	YES	YES	YES	28 days
Orthophosphorus	YES			48 hours

Summary of Nutrient Monitoring Methods

Method (Vendor and Catalogue #)	Approximate Cost	Monitoring Level Depends Upon DEQ Approval of QAPP (see Appendix 9)	Organizations Using Method
Nitrate Test Kits (LaMotte #3119, 3519, 3615, 3354; Hach #14161-00)	$53-$83	I	- Appomattox River Water Quality Monitoring Program (Clean Virginia Waterways / Longwood University) - Assateague Coastal Trust - Northern VA Soil & Water Conservation District
Ammonia Test Kits (LaMotte #3304 ; Hach #2241-00, 24287-00)	$55	I	- Alliance for the Chesapeake Bay - Assateague Coastal Trust
Nitrite Test Kits [LaMotte #7674 (50 tests) ; Hach #21820-00 (100 tests)]	$53-$79	I	- Northern VA Soil and Water Conservation District
Phosphate Test Kits [LaMotte #3121, 7416, 3119 (50 tests) ; Hach #2248-00, 2248-01 (100 tests)]	$65-$87	I	- Assateague Coastal Trust - Loudoun Soil and Water Conservation District
Colorimeter	$150-$1000	I	- Friends of Powhatan Creek Watershed
Lab	$7.50- $15.00 per sample per species*	I, II or III	- Friends of the Shenandoah River and affiliate organizations - Ferrum College (Smith Mountain Lake & Claytor Lake Programs) - Upper Rappahannock Watershed Stream Monitoring Project

*These costs are based upon submitting samples to the state laboratory, the Division of Consolidated Laboratory Services. This lab is only available to government organizations and nongovernmental organizations that receive state funding.